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Dynamic PEMFC model as a base for a state classifier and controller

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Abstract

Online state classification of PEM fuel cell systems is a challenging task. While electrochemical impedance spectroscopy (EIS), the measurement of the 1 kHz impedance, cyclic voltammetry, and the polarisation curve are the state-of-the-art in laboratory testing, it is hardly possible to install these analytic methods in application-oriented fuel cell systems. The necessary technical equipment is expensive, and hybridisation would be essential to create artificial operating conditions necessary during the measurement. A more economic solution for online state classification is the integration of a real-time model-based state classifier. A model, operating in parallel to the fuel cell, is able to provide extra information about the fuel cell such as the humidity of the membrane, which is not measurable in situ. On the other hand, online comparison of measurement data with the theoretical calculation allows us to detect malfunction of components. Based on a detailed model and a complex classification database, including error states of the system, it is possible to classify the state of a fuel cell or detect system errors. The voltage drift between classical physical models and a real fuel cell caused by irreversible degradation (platinum diversion, membrane thinning, carbon corrosion) and reversible degradation (contamination) is not yet completely understood, and therefore modelling so far remains imprecise. To avoid the misinterpretation caused by these constantly growing differences between the model and the reality, the described modelling approach has been focused on dynamic fuel cell reactions. Dynamic step responses of the fuel cell for abruptly changing operation conditions are being simulated in real time. The changing operation conditions may result from a real load cycle or, as for theses analyses, by forced stoichiometric steps. The comparison of the real and the simulated step responses is the basis for the state classifier and the controller to react. A conclusion of the series of measurement is shown, the model and its parameters are presented, and the opportunities of the state classifier and controller are discussed in this paper.

Keywords: Dynamic PEMFC model; Advanced controller; Classification

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1. Introduction

To run a PEM fuel cell system means to find a balance between the best conditions for the fuel cell and the power consumption of the system to achieve high efficiency and low degradation. Therefore it is necessary to control multidimensional linked operating parameters like stoichiometry, humidification, temperature, and purge cycle. Control is usually based on a huge number of sensors and measurement techniques, which are expensive and often unstable. The development of an advanced controller and state classifier is the goal of different R&D approaches at ZBT.

The observation of the cell voltage gives only a rough indication for the state of the cell. It has been observed, that dynamic hysteresis and strong reversible degradations do affect the cell voltage of real life systems with up to 35% performance loss (see Fig. 2). These influencing factors avoid the deeper interpretation of the cell voltage for advanced control. The interpretation of the cell voltage without any additional information is insufficient to develop a ‘state classifier’ to differentiate between shifts of the cell performance caused by reversible and irreversible degradation and error states of the cell or the system.

As a base for the advanced controller and state classifier, an online model has to be developed. The parallel operation of a real fuel cell and the online model enables:

- error detection,
- the classification of the error, and
- advanced control by using additional information like the humidity of the membrane provided by the model.

Within the work first a 1D physical model has been developed and a series of measurements for its parameterisation have been performed. In a second approach a mathematical model has been developed.

2. 1D physical model

The intended base for the online model is a 1D physical model, which means that a complete stack is reduced to one cell that is not segmented. This simplification is demanded by the necessary real-time simulation speed for the online model. A physical model has the advantage of physical intermediate values like partial pressures, humidity, or further media properties. These are often immeasurable or difficult and expensive to measure. The parallel operation of the physical model provides these values, and enables advanced control based on this additional information.

The basic structure of the physical model is shown in Section 2.1. The required estimation of the empirical parameters is described in Sections 2.2 and 2.3.

2.1. Basic structure of the 1D physical model

The 1D physical model consists basically of two sub-models for the cathode and anode flow fields: a sub-model for the membrane-electrode assembly (MEA), and a sub-model for the overpotentials. The sub-models are linked to each other and interact together (Fig. 1). They are described in Sections 2.1.1, 2.1.2, and 2.1.3. The description of each modelled physical relation is reduced to the conclusive equations to show their main interactions.

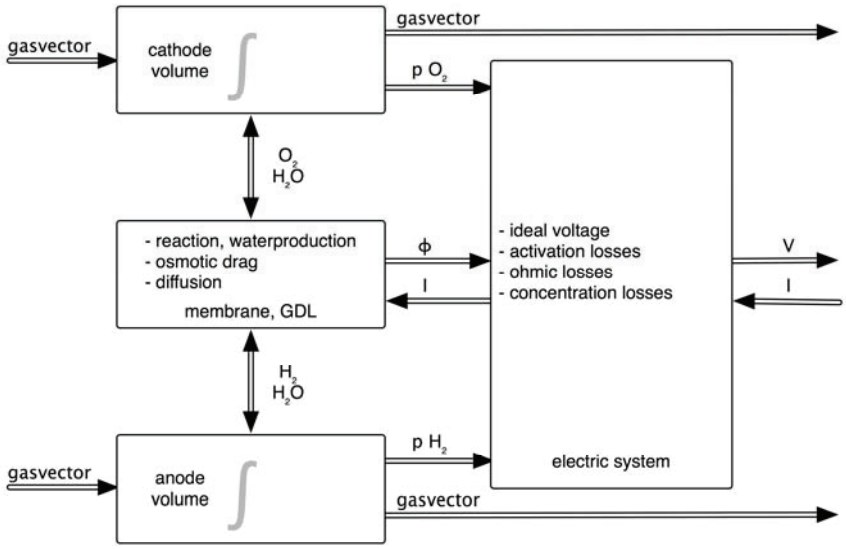

Fig. 1. Structure of the 1D physical model.

2.1.1. Cathode and anode volumes

The sub-models for the cathode and anode flow fields are based on a constant volume with defined in- and outgoing gases. The gas mix is described by the mass fraction of H_2, H_2O, O_2, and N_2. Along with the information on the temperature, pressure, and mass flow this information is combined to the 'gas vector'. The gas is treated as ideal gas. Separate volumes are used for the cathode and anode, the volume sizes correspond to the volume of the flow field channels.

2.1.2. MEA

The assembly of gas diffusion layer (GDL), microporous layer (MPL), electrode, and the membrane is modelled by a separate sub-model. The following interactions are described by the model:

- basic electrochemical fuel cell reaction;
- water content of the membrane; and
- water transport through the membrane driven by
  - electro-osmotic drag, and
  - diffusion.

The basic electrochemical reaction of the fuel cell reduces the amount of hydrogen in the anode sub-model, the amount of oxygen in the cathode sub-model, and adds the product water to the cathode. The calculation is strictly proportional to the fuel cell current.

The calculation of the membrane water content is based on the humidity of the cathode and anode. The average value of these is used for the computation of the membrane water content according to Um et al. [2].

The water transport through the membrane consists in the model of the osmotic drag and the water diffusion. The osmotic drag (eq. 1) is proportional to the stack current and the osmotic drag coefficient α_d is calculated according to Fuller [4]. The calculation of the water diffusion (eq. 2) is based on a diffusion coefficient D_l calculated according to Springer [1, 3] and the partial pressure difference of the water between the cathode and anode side of the fuel cell:

$$\dot{n}_{H_2O,osmotic} = \alpha_d \frac{I}{F} \tag{1}$$

$$\dot{n}_{H_2O,diffusion} = -D_l \Delta c_{H_2O} \tag{2}$$

The osmotic drag is driven by the proton flux through the membrane, and can only be calculated as the resulting water transport from the anode to the cathode. The diffusion is driven by the partial pressure difference of the water. The water flow can result from the anode to the cathode or the other way around. In the case of a resulting water flow from the cathode to the anode it is called ‘back diffusion’. This is the only possibility in the model to raise the amount of water on the anode side.

The equations include parameters such as the dry membrane weight or the membrane dry density. A first parameterisation can be done by values known from the literature and ex situ measurement. But it is possible to use these parameters for fine parameterisation of the model on measurement series. Measurement series have been done for this purpose, and are described in Section 2.2.

2.1.3. Overpotentials

The partial pressures H_2 and O_2 of the flow field sub-models, the humidity of the membrane, and the current of the fuel cell are the boundary conditions for the sub-model of the overpotentials. On the basis of the Gibbs free energy the ideal voltage is 1.229 V and the overpotentials are subtracted. Activation losses are determined by the Tafel law:

$$V_{actication} = \frac{R \cdot T_{fc}}{\alpha_{Tafel} \cdot F} \cdot \frac{I}{I_0} \tag{3}$$

The humidity of the membrane, calculated in the MEA sub-model, is the fundamental factor for the membrane resistance and the resulting ohmic losses:

$$V_{ohmic} = (\lambda_W \cdot \Delta M + \Omega_0) \cdot A_{act} \cdot I_{fc} \tag{4}$$

Finally, the calculations for the diffusion losses are based on the partial pressure of oxygen provided from the cathode flow field sub-model:

$$V_{diffusion} = \frac{R \cdot T_{fc}}{2 \cdot F} \cdot \log\left(1 - \frac{I \cdot \Delta y}{2 \cdot F \cdot D_{12} \cdot p_{O_2}}\right) \tag{5}$$

The model of the overpotentials is strictly static. No dynamic reactions or long-term shifts caused by reversible degradation of the fuel cell are modelled. Dynamic behaviour can only result from dynamically changing boundary conditions, e.g. by abrupt changes in incoming gases. The pressure calculation of the flow fields then determines a dynamic change of the related partial pressures. As the partial pressure is an input parameter for the model of the overpotentials, the voltage changes with the same dynamic as the

partial pressure of the flow fields. Another possible dynamic reaction results from a dynamically changing humidity of the membrane. The humidity of the membrane affects the ohmic resistance V_{ohmic} and the fuel cell voltage corresponds to the dynamic change of the humidity. These dynamic reactions of the flow field sub-model are limited to a few seconds. This means that, during static operation, it is not possible to compute voltage shift in the time scale with more than a few seconds at the beginning.

The equations include, just like the MEA sub-model, some empirical coefficients. and it is necessary to do some empirical parameter estimation. These parameterisations are described in Section 2.3.

2.2. Humidity screening for model parameterisation

Although the model is based on physical equations, there are several empirical parameters included in the equations. These parameters are necessary to adapt the model for different fuel cells, their components, and individual geometries. They can be parameterised roughly by values known from the literature, but they have to be improved empirically. The humidity balance of the fuel cell has a strong influence on the operation of the fuel cell. It is important to identify the empirical parameters in this sensible part of the fuel cell on a large base of measurement data. Extensive measurement series have been done for this purpose, and are named 'humidity screening'. The humidity screening has been done in a test rig with a two-cell fuel cell with 50 cm^2 active area. The educts, environmental air and pure hydrogen are dosed by mass flow controllers and humidified on defined dew points by bubble humidifier. The operation of the bubblers has been verified for the range of the tests. The off-gases from the fuel cell are cooled to 3°C, and the upcoming condensed water is collected and weighed. The water content of the cooled gas flow is treated as 100% humidified. The dry gas flow of the products is approximated by the educts and the basic electrochemical reaction of the cell. The difference in the incoming and outgoing gases is the resulting water flow through the membrane. The operation points are varied in a wide range. The cell is operated in crossflow mode.

Early analyses show significant water transport from the cathode to the anode (Table 1). The only possible water transport in the model from the cathode to the anode can be calculated in the case of back diffusion (Section 2.1.2). The back diffusion can only be driven by a higher partial pressure of the water on the cathode than on the anode side.

Table 1. Results of the humidity screening.

	Operation point					**Measurement data**					
#	stoic cathode	stoic anode	humidity air [%]	humidity H2 [%]	current [mA/cm^2]	humdity cathode off [%]	humidity anode off [%]	average humidity cathode [%]	average humidity anode [%]	water transport anode -> cathode [g/h]	error [%]
1	1.5	1.2	30	90	600	98.6	218.9	64.3	154.5	0.82	2.2
2	1.5	1.2	70	45	600	102.9	245.0	86.5	145.0	–8.43	6.3
3	1.5	1.2	30	30	800	84.1	206.7	57.0	118.3	–6.05	–2.2
4	1.5	1.2	50	60	800	98.0	234.2	74.0	147.1	–6.36	2.5
5	1.5	1.2	50	75	1000	101.5	235.4	75.8	155.2	–5.29	–0.7
6	1.5	2	0	60	200	81.1	91.4	40.6	75.7	0.46	4.8
7	1.5	2	0	75	400	84.2	105.1	42.1	90.0	1.58	2.5
8	2	1.2	10	90	200	85.5	35.2	47.8	62.6	2.83	5.9
9	2	2	70	30	200	88.1	147.1	79.0	88.6	–4.20	8.4
10	2	2	30	60	400	79.1	105.7	54.6	82.8	–0.54	1.4
11	2	2	90	75	800	101.5	176.8	95.7	125.9	–16.46	4.8
12	3	1.2	10	30	400	51.2	41.9	30.6	36.0	1.24	–10.3
13	3	2	10	75	600	57.7	78.8	33.9	76.9	5.98	–7.3

The measurement results listed in Table 1 all show a higher average partial pressure of water on the anode side than on the cathode side. But the measurement points 2, 3, 4, 5, 9, 10, and 11 show a resulting water transport from the cathode to the anode, a back diffusion which occurs at least in parts of the active area. The resulting water flow at these operation points is incalculable with the presented 1D physical model, since the gradient of the partial pressure of water and the resulting water transport disagree. In general, it is not possible to build a 1D model that fits to the measurement data shown in Table 1. It might be possible with a 2D model, which allows differentiation of the water exchange in dry and wet areas of the cell area.

2.3. Stationary cell operation for model parameterisation

The fuel cell has been operated for each operation point of the humidity screening (Table 1) for several hours stationary. These measurement data should be able to be used for the parameterisation of the overpotential sub-model. But the measurement series do show a strong reversible degradation. Up to 5% performance loss is measured within the first 12 hours after the beginning of the test (Fig. 2). The sub-model of the overpotentials cannot be fitted to these measurement data. A reversible degradation is not included in the model (Section 2.1.3).

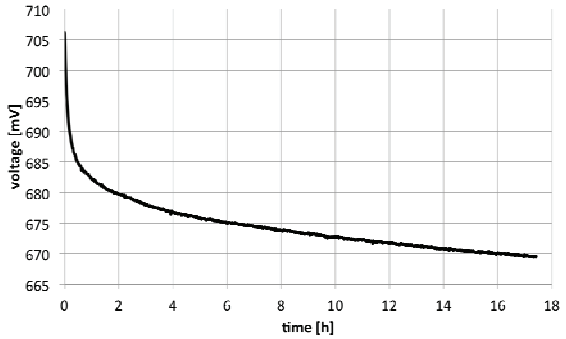

Fig. 2. Exemplary reversible fuel cell degradation (400 mA/cm^2, 70°C; cathode RH = 0%, stoich. 1.7; anode RH = 76%, stoich. 4.9).

This degradation is caused by internal and external contamination and drying out of the membrane in the inlet region of the cathode. Compared to, for example, the influence of the membrane water content on the ohmic losses or the influence of the partial pressure of the oxygen on the diffusion losses, this is significant and not negligible.

The effects are identified, well known, and they do affect the fuel cell, but the quantity and time behaviour of each particular effect is unknown. It is necessary to integrate these effects into the model. Reversible degradation affects the fuel cell during the operation time with a different intensity. The drying out of the cell affects a wet fuel cell much more than a fuel cell that is already dried out. Consequently is it necessary to define the humidity of the fuel cell at the start of a simulation. In the case of an online simulation, synchronisation between the model and the real fuel cell is required at the beginning of the simulation. The synchronisation would initialise the time-dependent coefficients. This is possible, if only one time-dependent coefficient has to be synchronised and the remaining operation conditions are known. This is not possible if several coefficients have to be synchronised.

Thus the strong reversible degradation prevents a reliable online simulation. Within the project consortium 'Life time prediction' models and parameterisation for cell degradation are being developed. Based on these results, the degradation mechanism will be integrated into the model.

3. Mathematical model

Since the 1D physical model is not targetting the requirements for the online model, an alternative approach is realised.

3.1. Stoichiometric step response

A highly sensitive response on stoichiometric steps has been observed during the measurement series for the 1D physical model (Fig. 3). Different stoichiometries lead to different partial pressures of the educts.

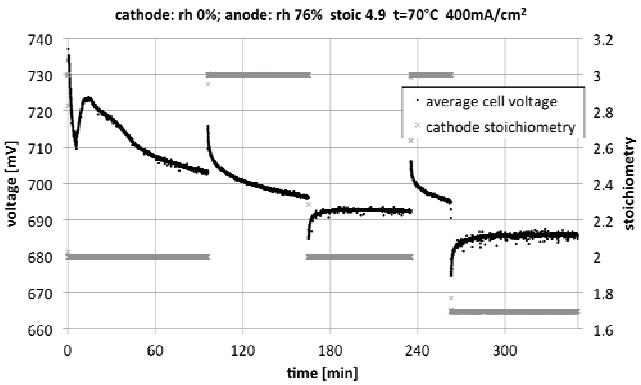

Fig. 3. Voltage step responses on stoichiometric jumps of the cathode supply.

A step in the stoichiometry from 2 to 3 on the cathode side causes a step in the average partial pressure of oxygen from approximately 8% to 14.3% of the whole pressure. The partial pressure of oxygen is part of the overpotential calculation of the activation losses and the diffusion losses (eqs. 3, 5). The activation losses significantly affect the cell voltage at a very low fuel cell current, whereas the diffusion losses significantly affect the cell voltage at high fuel cell currents. The step responses on the stoichiometric variations have been observed at a medium current, 400 mA/cm^2. It is not possible to reproduce these step responses with the 1D physical model of the activation losses or the diffusion losses. Even with specially adapted empirical coefficients of the equations, it is not possible to reproduce the shown step response.

These observations lead to a more detailed view on the phenomena, and thereby the resulting analysis options.

3.2. Background

A series of additional measurements has been done to visualise the reason for the observed voltage responses. The stoichiometric step responses have been applied to a cell with a segmented bipolar plate. Thus it is possible to measure the distribution of the current across the active area of the cell. The segmentation consists of 8 × 16 segments for an active area of approximately 5 × 10 cm. The cathode

supply is dry with variations in the stoichiometry. The anode supply is fixed with a stoichiometry of 4.9 and a relative humidity of 76% calculated on the cell temperature of 70°C. The overall current is set to 400 mA/cm^2.

The displayed current contribution is not converted to current densities, and the absolute current is the unit. The border segments of the segmented cell do not have the same size as the inner segments, which results in imprecise data at the border segments. The inner segments have a size of 0.39 cm^2. The flow direction of the cathode is from bottom to top, while the anode flow direction is the other way around.

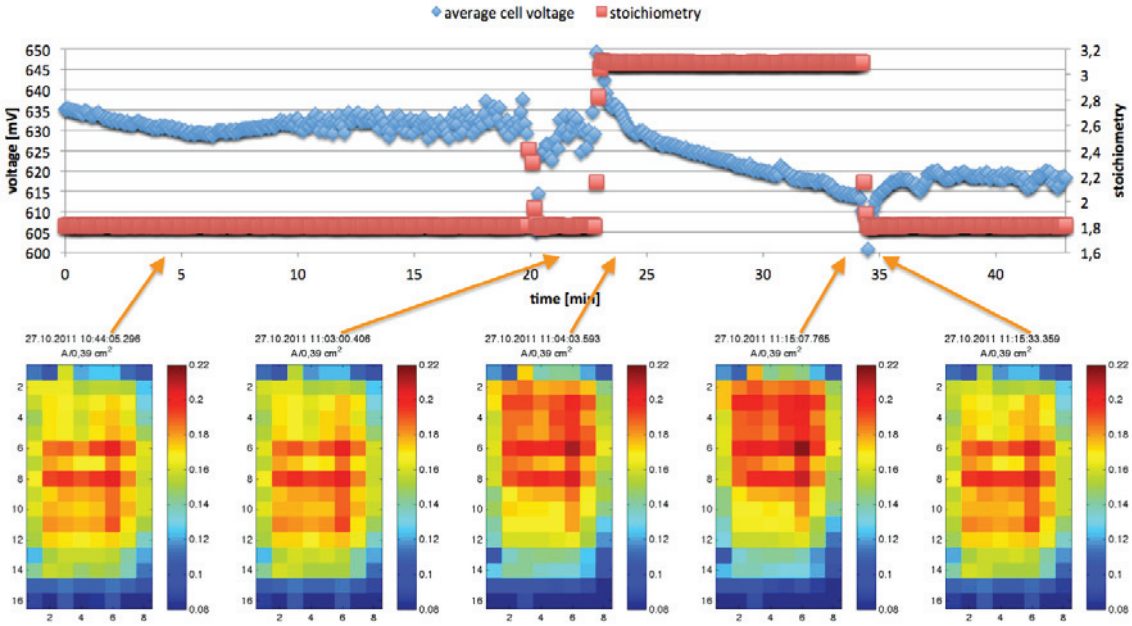

Fig. 4. Segmented measurement series – shift of the most active region.

The stoichiometric variation causes a shift of the most active region (Fig. 4). The inhomogeneous humidity of the cell then causes, in combination with the shift of the most active region, the step response of the cell. In the case of the stoichiometric step from 2 to 3, the most active region is shifted to a region where the cell is well humidified. The previous operation point with the stoichiometry of 2 causes this good humidification. At a stoichiometry of 2 the humidity increases from approximately 0% RH (relative humidity) at the inlet to 65% RH at the outlet of the cathode. The operation point with the stoichiometry of 3 leads to a much drier fuel cell. The humidity increases from approximately 0% RH at the inlet to 44% RH at the outlet. The cell dries out faster during the operation with a stoichiometry of 3. But directly after the stoichiometric step from 2 to 3, the humidity of the membrane is still on the level of the previous operation point, and the positive voltage reaction results.

3.3. Series of measurements

Series of measurements have been done to analyse the correlations of the step responses. Each measurement series is performed for one set of anode stoichiometry and dew point. The cathode supply is

dry and the stoichiometry varied between 2 and 3. The cell temperature and current are set to 70°C and 400 mA/cm^2, respectively. The measurement has been performed with a two-cell short stack operated in crossflow mode. The variation of the stoichiometry is realised with an incremental step size of the stoichiometry. After a couple of hours of continuous operation at a stoichiometry of 2, steps with a stoichiometry of 3 are induced for 1, 5, 15, and 90 minutes. Between these operation times with a stoichiometry of 3 the cell has been operated for 5 minutes at a stoichiometry of 2. This procedure is reversed after approximately 3.5 hours. On the basis of the stoichiometry 3 steps are induced with a stoichiometry of 2 for 1, 5, 15, and 90 minutes. Fig. 5 shows the anode conditions for each measurement series, and Fig. 6 part of the schematics of the stoichiometric step cycle. The results of the whole measurement series are shown in Fig. 7. The measurement series with the dew point 62.5°C have been stopped in between. They have been operated for a few hours at a stoichiometry of 3, before the stoichiometric step series have been induced in the second half.

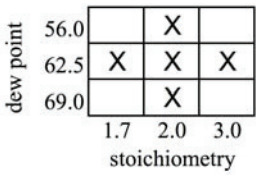

Fig. 5. Anode operating conditions for each measurement series.

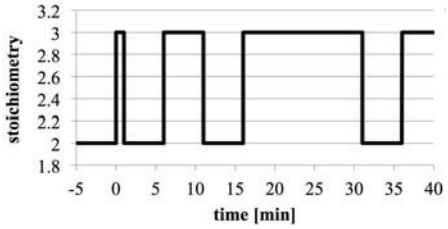

Fig. 6. Stoichiometric step cycle.

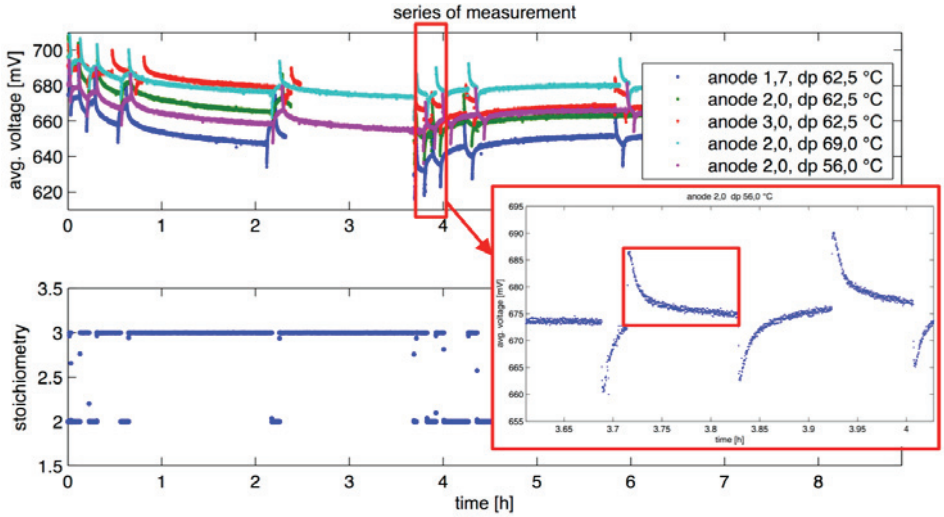

Fig. 7. Measurement series with individual anode operating conditions and stoichiometric steps on the cathode side.

3.4. Mathematical analysis

The step responses of the cell voltage all have similar shapes, but differ in their individual magnitude and speed. Analyses of every step response have been done mathematically to quantify the individual

characteristic. They have been fitted with the function f_{sr} (f_{sr} = function of the step response), which consists of two combined exponential functions (f_a, f_b):

$$f_{st}(t) = f_a(t) + f_b(t) \tag{6}$$

$$f_a(t) = A(1 - e^{-\frac{t}{a}}) \tag{7}$$

$$f_b(t) = B(1 - e^{-\frac{t}{b}}) \tag{8}$$

The factors A, B, a, and b are set for fitting such that f_a fits to the degression after the step response and f_b describes the immediate step response (Fig. 8). A and B describe the magnitude of the immediate step response and the degression. To fit these parts A and B have to be set corresponding to the particular direction of the step response, they have to be preset with opposite signs. The factors a and b describe the rate of the immediate step response and the degression. For the fitting the factor a has to be set around 25 times higher than the factor b. The curve fit has been done by GFaI (Society for the Promotion of Applied Computer Sciences) in Berlin.

It is hardly possible to derive information about the fuel cell directly out of these factors. The factors only fit in their collectivity. But it is possible to derive information out of the combined functions f_{sr}, f_a, and f_b with further analysis. The most significant information on the step response is calculated by the sum of the magnitude of the immediate step response Y_{max} and the inversed degression after 60 seconds $f_a(60) \rightarrow (Y_{max} - f_a(60))$.

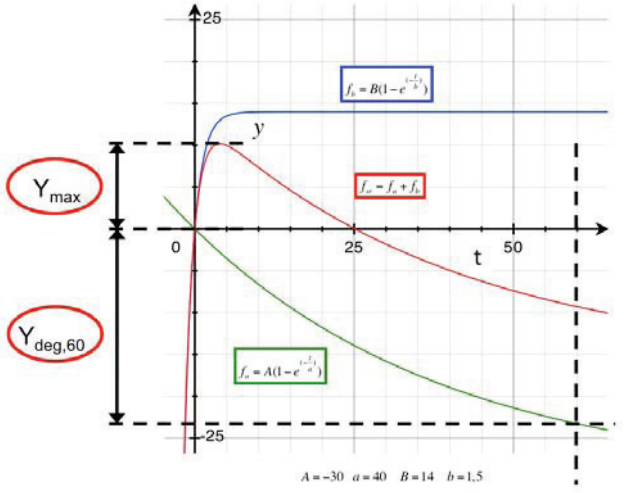

Fig. 8. Combined exponential functions and calculation base for the characteristic factor.

3.5. Results

This characteristic factor (Y_{max} – $f_a(60)$) cannot be directly correlated with a specific operation condition of the fuel cell, but the factor can be correlated with the general state of the cell, and is named the ‘Feel Good Factor’ (FGF). The smaller the absolute value of the Feel Good Factor, the better is the fuel cell state.

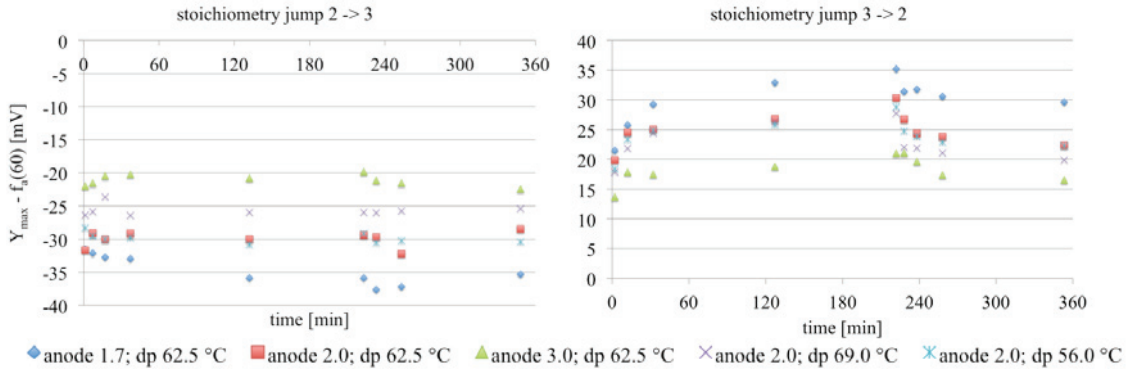

Fig. 9. 'Feel Good Factor' analysis.

The results are conclusive in themselves. Better anode humidification leads to better fuel cell performance and a smaller FGF. Equally, a larger anode stoichiometry leads to better fuel cell performance and a smaller FGF (Fig. 9). Furthermore, each measurement series is conclusive in itself. During the first half of each measurement series the operation time with the stoichiometry 3 increases and the cell dries out. The FGF increases during that time. In the second half of each measurement series the time with a cathode stoichiometry of 2 increases again. The average humidity on the cathode side with a stoichiometry of 2 is higher than at the stoichiometry 3 and the cell humidifies itself. The FGF again decreases in the second half of the measurement series.

3.6. Conclusion for the mathematical model

The Feel Good Factor gives stable information about the general state of the fuel cell. It can be achieved without any information about the history or any initialisation procedures. The noisy fuel cell voltage is so far no problem for the measuring method.

At present there are some limitations for the measuring method. It is necessary to operate the fuel cell for at least 30 seconds (or better, 1 minute) constantly. But it is theoretically possible to apply the analytical stoichiometric step to a dynamically operated system. Analysis could then be done on the step response of the floating polarisation curve. Furthermore, only a few operation points have been analysed with the Feel Good Factor so far. The current and cell temperature are fixed and the reviewed media supplies are rare. Further analyses have to be done.

4. Conclusions

The attempt to build a physical model with real-time ability has failed. The 1D simplification prevents calculation of the humidity balance that is essential for low-temperature PEM fuel cells. Furthermore, strong time-dependent reversible degradation has been obtained. Since multiple effects cause the reversible degradation, like drying out of the cell or contamination, multiple time-sensitive coefficients have to be synchronised. This is not possible if only one measurement signal, the fuel cell voltage, is available for the synchronisation.

However, mathematical analysis of the fuel cell step response on a stoichiometric step of the cathode supply do have the possibility to be used for online analysis. The calculation of the Feel Good Factor (FGF) can be performed without any synchronisation or knowledge of the history. It has been shown that the FGF describes effects like the reversible degradation caused by drying out, and that the FGF describes the general state of the fuel cell.

Acknowledgments

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